Preface

Two technologies, namely L*aser Technology* and *Surface Modification Technology*, have made rapid strides in the last few decades. The lasers have evolved from a simple laboratory curiosity to a matured industrial tool and its applications are limited only by imagination. Intense, coherent and monochromatic laser sources with power outputs ranging over several orders of magnitude have found innumerable applications in the realm of materials engineering. Reactive Pulsed Laser Deposition (PLD) is a powerful technique that utilises the power of a nanosecond pulsed laser for materials synthesis. Unlike conventional PLD, which require high density targets that are difficult to synthesize at a reasonable cost, the RPLD circumvents the need for one such ceramic target. This thesis presents a detailed and judicious use of this technique for synthesis of hard ceramic multilayer coatings using elemental metal targets.

Transition metal nitrides having rock salt structure are known to exhibit superior properties such as hardness and wear resistance and hence formed the basis for the development of first generation coatings. Further improvements through alloying of these binary compounds with metal or metalloid components lead to the development of second generation coatings. As the demand for functional materials increased, *surface modification technology alias surface engineering*, grew in leaps and bounds. As the large number of coating requirements for optimal performance could not be fulfilled by a single homogeneous material, third generation coatings, comprising multilayer coatings, were developed. It is this aspect of combining the advantages of RPLD process to synthesize ceramic multilayer coatings, provides the main motivation for the present research work.

In this thesis, a systematic study presented for synthesis of nanocrystalline and stoichiometric TiN and NbN thin films using RPLD through ablation of high purity titanium and niobium targets, in the presence of low pressure nitrogen gas. A novel Secondary Ion Mass Spectrometry (SIMS) based analysis was developed to effectively deduce the important process parameters in minimum trials to arrive at desired composition. The validity of this SIMS based method, for optimization of process parameters to get stoichiometric nitride films, was proved beyond any speculation by corroborative Proton Elastic Backscattering Spectrometric (PEBS) analysis. SIMS was also used to characterize the [NbN/TiN] multilayers. The feasibility of growing nanocrystalline multilayers with varying thicknesses has been demonstrated. Nanomechanical properties including hardness and adhesion strength of monolithic TiN and NbN films and multilayers were evaluated.

The thesis is organised into six chapters. The first chapter gives a brief account on the history and development of '*surface engineering*'. The second chapter provides a comprehensive description of the experimental facility developed in-house to pursue research on PLD grown ceramic thin films and multilayers. Thin film synthesis procedure for ex-situ SIMS and TEM analyses is described. Brief introduction is also presented on the characterization techniques used in this study to investigate the surface, interface and microstructural aspects of PLD grown films with underlying basic principles. The third and fourth chapter describes the synthesis and characterization of titanium nitride and niobium nitride thin films using RPLD technique, respectively. SIMS was used in depth profiling mode, for optimization of three important process parameters, viz., nitrogen gas pressure, substrate temperature and laser pulse energy, to get stoichiometric nitride films. Further, films were characterized using GIXRD, TEM, XPS and PEBS for their structure and composition. AFM measurements were made to elucidate the surface morphological features. PEBS was effectively used to estimate the nitrogen concentration in a quantitative manner and the results corroborate well with the SIMS measurements. Having succeeded in synthesizing stoichiometric TiN and NbN films, further studies on the nanomechanical properties of monolithic TiN and NbN films and their multilayers were carried out and these results form the contents of the fifth chapter. The findings of the work reported in this thesis are concluded in Chapter 6 and few possible suggestions were presented as future directions.

Both the monolithic TiN and NbN coatings showed a deposition pressure dependent hardness variation. The hardness of these monolithic films was found to be around 30 GPa, higher than the hardness values obtained by other conventional techniques. Keeping total thickness of the multilayers constant at 1 μm, [NbN/TiN] multilayers having bilayer periods ranging from 50 nm to 1000 nm, were synthesized. A systematic enhancement in hardness upto ~ 40 GPa was observed for $[NbN/TiN]_{10}$ with the modulus of the multilayer remaining almost constant. The pileup observed around the indentation edge is indicative of toughening in multilayers. The tribological properties of multilayer films showed a better performance in terms of low coefficient of friction and regeneration of coating surfaces as revealed from the nanotribological studies. Overall, the multilayer coatings exhibited better performance in terms of hardness, toughness and adhesion with the substrate material.